

EVALUATION OF THE EFFECT OF SCR ON MERCURY SPECIATION AND EMISSIONS

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ABSTRACT

Since the U.S. Environmental Protection Agency's determination in 2000 that it intended to regulate mercury emissions from coal-fired power plants, many utilities have taken proactive steps to investigate methods to control and reduce emissions. However, a lack of data still exists to document the effect of selective catalytic reduction (SCR) on the speciation and removal of mercury (Hg) at power plants. Although SCR systems are effective at nitrogen oxide reduction, such systems may impact mercury speciation differently.

This project investigates the impact that SCR has on total mercury emissions and on the speciation of mercury. If SCR systems enhance mercury conversion/capture, then they can be used as multipollutant technologies. Previous Energy & Environmental Research Center pilot-scale tests investigated the role that coal type plays in mercury speciation with the addition of ammonia (NH₃) and the use of SCR. The results indicated that SCR and NH₃ may enhance mercury oxidation, although it appeared that the impact was highly coal-specific and so concerns were raised as to the applicability of the pilot-scale results to full-scale power plants.

To investigate the role of SCR in mercury speciation, Hg measurements were completed at seven different power plants, four in 2001, two in 2002, and one in 2003, that were equipped with SCR. In addition, two of the plants tested in 2001 were retested in 2002 for a total of nine data sets.

Sampling was conducted to evaluate the effect of SCR operation by testing both with and without the SCR in operation. This was accomplished by bypassing the SCR or by testing sister units, one with and one without SCR. Hg sampling was conducted using the manual Ontario Hydro (OH) method and Hg semicontinuous emission monitors (Hg SCEMs). The

sampling plans were set up to obtain OH samples at the SCR inlet and outlet, ESP inlet and outlet or, in the case of one plant, a venturi scrubber, and at the stack. The Hg SCEMs were used to measure Hg speciation primarily at the outlet of the particulate control device. Fly ash and coal samples were also collected to obtain the Hg balance across the control devices.

For plants firing eastern bituminous coals, there was an increase in Hg oxidation across the SCR catalysts. The effect SCR has on Hg speciation (i.e., extent of additional oxidation that occurs) is apparently dependent upon the coal characteristics and catalyst properties.

INTRODUCTION

Coal combustion by electric utilities is a large source of anthropogenic mercury emissions in the United States, according to the U.S. Environmental Protection Agency (EPA).¹ Recent data indicate that the total mercury emissions from coal-fired power plants in the United States are about 45 tons/yr.² EPA views mercury from coal-fired utilities as a potential public health concern and, as a result, is currently involved in a rule-making process.³

Mercury emissions from coal-fired boilers can be empirically classified, based on the capabilities of currently available analytical methods, into three main chemical forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle-bound mercury (Hg_p). The concentration of Hg^0 , Hg^{2+} , and Hg_p in the flue gas primarily depends on coal composition and combustion conditions.⁴

During combustion, Hg^0 is liberated from coal. However, depending on the coal type, a significant fraction of the mercury can be oxidized, as well as become associated with the fly ash particles in the postcombustion environment of a coal-fired boiler. Relative to Hg^0 , the Hg^{2+} and Hg_p are more effectively captured in conventional pollution control systems, such as flue gas desulfurization (FGD) systems, fabric filters, and electrostatic precipitators (ESPs).⁵⁻⁷ The identification of a process for converting Hg^0 to Hg^{2+} and/or Hg_p forms could potentially improve the mercury removal efficiencies of existing pollution control systems.

In addition to mercury, coal-burning power plants are a significant anthropogenic source of nitrogen oxide (NO_x) emissions to the atmosphere. NO_x emissions are an environmental concern primarily because they are precursors to acid precipitation and are involved in atmospheric reactions that produce fine particles ($\text{PM}_{2.5}$) and ozone. With the possible establishment of more strict ozone regulations and $\text{PM}_{2.5}$ and regional haze requirements, there is increased incentive to reduce NO_x emissions to a level below what is currently being achieved. Selective catalytic reduction (SCR) technology, which can reduce NO_x emissions by >90%, is therefore becoming more attractive, particularly because catalyst costs continue to decrease and the knowledge base for using SCR reactors is expanding. It is planned that approximately 100 gigawatts of coal-fired capacity will have SCR for NO_x by 2005.⁸

Pilot- and full-scale testing in both the United States and Europe has indicated that SCR catalysts can promote the formation of Hg^{2+} .⁹⁻¹¹ Therefore, the use of SCR to reduce NO_x emissions may improve the mercury control efficiency of existing air pollution control devices by promoting Hg^{2+} formation.

Beginning with pilot-scale tests in 2000,¹² EPRI, the U.S. Department of Energy's National Energy Technology Laboratory, EPA, and a number of utilities have funded a project with the Energy & Environmental Research Center to conduct mercury sampling to determine the impact of SCR technology on mercury speciation for a range of plant configurations and coal types.

To date, Hg sampling has been completed at seven different power plants equipped with SCR. Four plants were tested in 2001, two in 2002, and one in 2003. In addition, two of the plants tested in 2001 were retested in 2002 for a total of nine data sets.

The units tested ranged from 650 to 1300 MW in size. The coals burned at the plants included one Powder River Basin (PRB) coal, four eastern bituminous coals, one low-sulfur eastern bituminous coal, and one PRB–eastern bituminous blend. The plant configurations of air pollution control devices included SCR reactors, ESPs, wet FGD systems, and a combined particulate–SO₂ venturi scrubber. Information regarding the configuration of each plant is provided in Table 1. The coal analysis for each unit tested is shown in Table 2. It should be noted for the purposes of this paper that the results from the PRB plant (S1) are not presented. The plant had a cyclone boiler and generated ash with a high level of unburned carbon (>15%). As a result, there was a substantial percentage of Hg_p, both with and without the SCR.

EXPERIMENTAL APPROACH

The overall objective of the project was to determine the impact of SCR operation on Hg speciation and, ultimately, on Hg emissions. To achieve this objective for each unit/coal, a sampling plan was developed for various operating conditions so that the effects of SCR could be determined. At each site, tests were conducted (where feasible) under operating conditions with and without SCR. This was done either by bypassing the SCR system or by testing sister units, one with and one without SCR.

In addition to the effects of SCR operation, several other factors were identified as possible contributing factors to Hg oxidation and removal. These factors included coal type, specifically chlorine and sulfur content, and catalyst age.

For each unit tested, sampling with the Ontario Hydro (OH) mercury speciation method was completed across each of the existing air pollution control devices to evaluate the effect of the device. In addition, Hg semicontinuous emission monitors were used to measure Hg speciation at the outlet of the particulate control device. Fly ash and coal samples were also collected to obtain the mercury balance across the control devices.

RESULTS AND DISCUSSION

Mercury Oxidation Across the SCR Catalyst

The percentage of Hg²⁺ was measured at both the inlet and outlet of the SCR at each facility, including the unit where a PRB–bituminous blend is used. For all of the plants tested, with

Table 1. Summary of SCR plant configuration.

Plant	Coal	Boiler Type	Boiler Size, MW	Low-NO _x Burners	Catalyst Vendor And Type	Catalyst Age	SCR Space Velocity, hr ⁻¹	Particulate Control	Sulfur Control
S1 ¹	PRB subbit.	Cyclone	650	No	Cormetech honeycomb	2 ozone seasons	1800	ESP	Low-sulfur coal
S2	OH bit.	Wall-fired	1300	Yes	Siemens/Westinghouse plate	3 months	2125	ESP	Wet FGD
S2-2 ²	OH bit.	Wall-fired	1300	Yes	Siemens/Westinghouse plate	2 ozone seasons	2125	ESP	Wet FGD
S3	PA bit.	Tangential-fired	750	Yes, with overfire air	KWH honeycomb	1 ozone season	3930	ESP	None
S4	KY bit.	Cyclone	650	No	Cormetech honeycomb	1 ozone season	2275	Venturi scrubber	Venturi scrubber
S4-2 ²	KY bit.	Cyclone	650	No	Cormetech honeycomb	2 ozone seasons	2275	Venturi scrubber	Venturi scrubber
S5	WV bit.	Wall-fired	684	Yes	Halder-Topsoe plate	3 months	3700	ESP	Wet FGD
S6	Low-sulfur KY and WV bit.	Concentric-fired	700	Yes	Cormetech honeycomb	2 ozone seasons ³	3800	ESP	None
S8	60% PRB/40% Eastern bit.	Wall-fired	820	Yes	Cormetech honeycomb	3 months	3100	ESP	None

¹ Not discussed in detail in this report.² Plant was retested in 2002.³ One layer of catalyst was replaced after one ozone season.**Table 2. Summary of coal analyses for plants tested, on a dry basis.**

	S1	S2	S2-2 ¹	S3	S4	S4-2 ^{1,2}	S5	S6	S8
Mercury, µg/g	0.10	0.17	0.14	0.40	0.13	0.18	0.13	0.07	0.07
Chlorides, µg/g	<60	1330	520	1250	360	270	470	1020	790
Moisture, %	27.5	7.6	6.1	7.0	10.5	8.3	4.6	6.1	25.9
Ash, %	4.76	12.6	10.0	15.0	10.1	9.9	12.7	12.3	5.9
Sulfur, %	0.24	4.2	4.1	1.8	3.2	3.2	3.8	1.1	0.88
Heating Value, Btu/lb	11,446	11,934	12,835	12,220	12,531	13,080	12,677	12,752	12,869

¹ Site tested in 2002 that had previously been tested in 2001.² Coals appear to be somewhat different (first coal was used during SCR operation, the second during SCR bypass).

the possible exception of Site S3, there was an increase in Hg oxidation across the SCR catalyst; however, the extent of additional oxidation was highly variable. It is suspected that the level of oxidation is affected by coal composition, catalyst chemistry and structure, and catalyst age. A summary of the results illustrating the percent of Hg^{2+} at the SCR inlet, SCR outlet, and particulate control device inlet locations is provided in Figure 1.

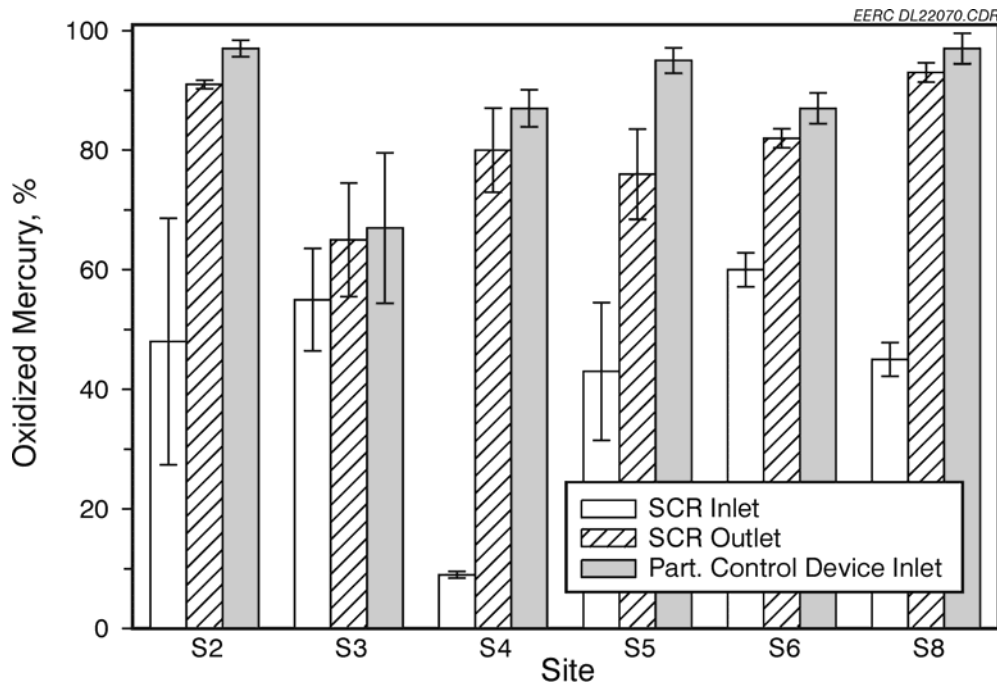


Fig. 1. Effect of the SCR catalyst on mercury speciation.

Once flue gas enters the SCR system, it would be expected that other factors such as catalyst type, structure, and space velocity might impact Hg oxidation; however, insufficient data have been generated to determine these interactions. For example, Sites S2 and S4 had space velocities less than $2,300 \text{ hr}^{-1}$, while Sites S3, S5, and S6 had space velocities greater than $3,700 \text{ hr}^{-1}$ (Table 1); however, no correlation is evident.

Overall Effect of SCR on Mercury Speciation

Strong evidence exists that an SCR system does promote mercury oxidation; however, the overall impact across the entire boiler system is also of interest. To evaluate the net effect of SCR operation on mercury speciation, measurements were conducted at the particulate control device inlet, both with and without SCR operation. Figure 2 provides a summary of nonelemental mercury results from these tests. At Sites S2, S4, S5, and S8, a greater quantity of nonelemental mercury was measured when the SCR was operating; at Sites S3 and S6, statistically no change occurred. However, at Sites S3 and S6, $>90\%$ nonelemental mercury was measured when the SCR system was not in service.

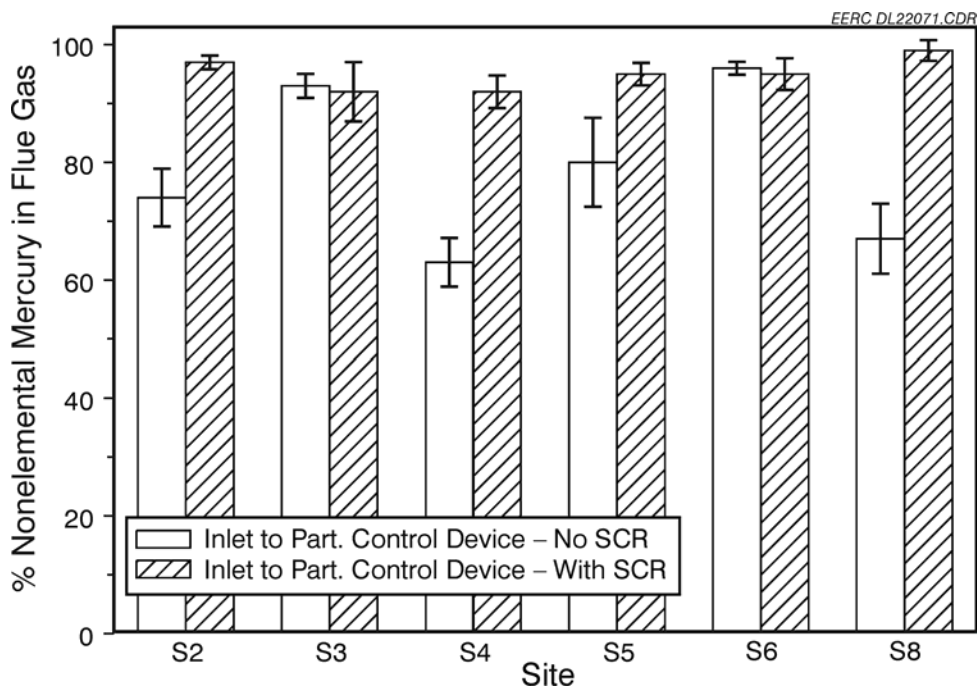


Fig. 2. Overall effect of the SCR on mercury speciation.

Effect of Catalyst Age on Mercury Speciation

Flue gas monitoring was conducted over 2 consecutive years at two power plants to evaluate the impact catalyst age had on mercury speciation. Sites S2 and S4 were tested in both 2001 and 2002 to determine if the oxidation potential of SCR catalysts was reduced with time, specifically after one additional season of operation.

As illustrated in Figure 3, a decrease in mercury oxidation occurred at Site S4, between 2001 and 2002, as measured across the SCR system. At Site S2 the results were the same in 2001 and 2002, within the variability of the data. However, at both sites at the particulate control device, the overall extent of oxidation was essentially unchanged after an additional season of SCR operation.

It is possible that catalyst life impacts oxidation potential, however, mitigating circumstances at each plant make the results inconclusive. At Site S2, humidification and alkali injection were done upstream of the SCR system, reducing the SCR temperature by approximately 10°F in 2002 compared to 2001. Additionally, at both plants, the coal burned in 2002 appeared to be somewhat different from that used in 2001.

Effect of SCR Oxidized Mercury at Wet FGD

The underlying intent of understanding SCR-mediated Hg oxidation is to determine its potential to improve the Hg collection efficiency of existing ESPs, fabric filters and, in particular, FGD systems on a sustainable basis. In general, wet FGD systems remove a large percentage (>90%) of Hg^{2+} . However, there has been evidence that some of the captured

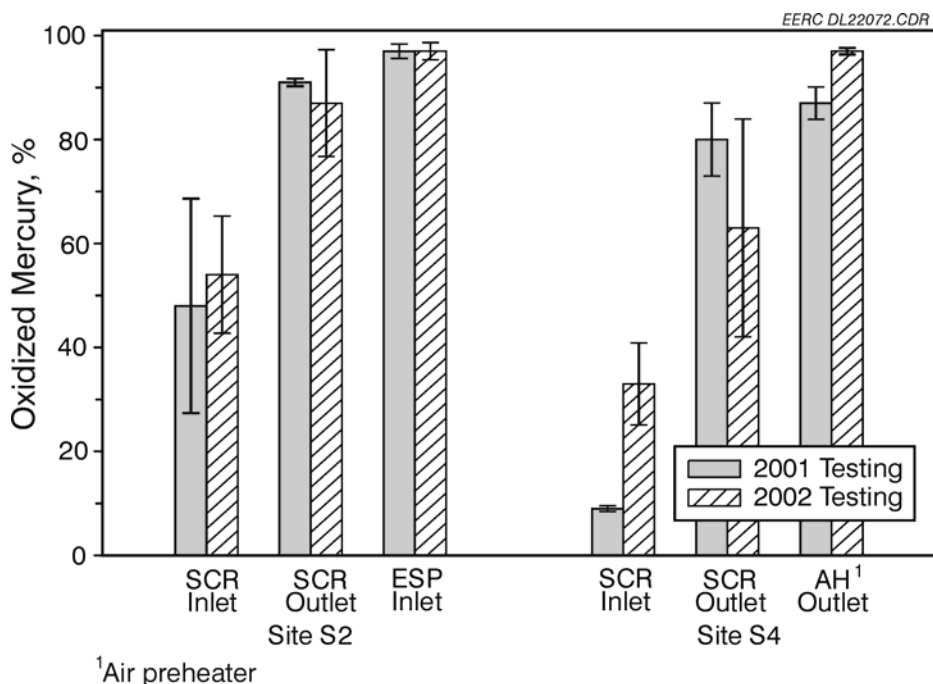


Fig. 3. Effect of SCR catalyst aging on mercury speciation.

Hg^{2+} can be reduced in the wet FGD system to Hg^0 .¹³ The sample set is very small (three facilities), and the wet FGD systems tested, to date, are not representative of the fleet of wet FGD systems that have been installed at power plants across the nation. For example, two are magnesium-enhanced lime FGD units, and the other is a combined particulate- SO_2 venturi-spray tower scrubber. By contrast, ~60% of the wet FGD systems in the United States are limestone forced-oxidation systems. The data from this project tend to indicate some type of Hg reemission is occurring. As can be seen in Table 3, at all the sampling sites, there is an increase in Hg^0 across the scrubber. Also, the data seem to indicate that the operation of the SCR system mitigates the effect.

Table 3. Effect of SCR on mercury reemission from a wet FGD system.

Plant	Year Sampled	FGD Inlet Hg^0 Conc., $\mu\text{g}/\text{Nm}^3$	FGD Outlet Hg^0 Conc., $\mu\text{g}/\text{Nm}^3$	Hg^0 Increase, $\mu\text{g}/\text{Nm}^3$	Total Hg Removal, %
With SCR					
S2	2001	0.4	0.9	0.5	89
S2	2002	0.3	1.3	1.0	84
S4	2001	0.5	0.8	0.3	90
S4	2002	1.0	1.3	0.3	91
S5	2002	0.7	1.0	0.3	91
Without SCR					
S2 ¹	2001	3.4	5.0	1.6	51
S4	2001	5.6	7.1	1.5	46
S4	2002	5.7	8.0	2.3	44
S5	2002	4.7	6.1	1.4	51

¹ S2 and S5 are magnesium enhanced lime scrubbers and S4 is a combined particulate and SO_2 venturi scrubber.

CONCLUSIONS

The observations from these data are as follows:

- For plants firing eastern bituminous coals, Hg oxidization occurs across the SCR catalysts. However, it appears to be variable and most likely related to a variety of factors. Some potential factors are coal characteristics, catalyst chemistry, catalyst type and structure, space velocity, and catalyst age.
- With the exception of Site S3 (where the Hg was essentially all Hg^{2+} or Hg_p , both with and without SCR), all facilities showed increased oxidation at the inlet to the particulate control device, ranging from 15% to 39%.
- At Site S4, there appeared to be a slight decrease in Hg oxidation across the SCR catalyst between one and two ozone seasons of operation. At Site S2, the results were essentially the same in 2002 as they were in 2001. However, other possible explanations related to changes in plant operation existed that might explain the results. These changes do not allow a definitive conclusion to be reached concerning the effect of an additional ozone season on SCR/Hg oxidation. It is important to note that the Hg oxidation at the inlet to the particulate control device is not affected by the age of these catalysts.
- Based on the limited data at three plants (five total data sets), it appears that some reemission of the captured Hg occurs across the wet FGD systems. For the tests with SCR in service, the increase appears to be very small and is generally within the variability of the data. Nevertheless, five data points show an increase in Hg^0 . When SCR is not present, it appears that the reemission is more pronounced.
- The use of SCR when firing a nominal 60%–40% blend of PRB and eastern bituminous coal resulted in increase mercury oxidation. However, this is only one data set.

FUTURE TEST PLANS

Based on a review of these test results, plans are being made for additional testing to more fully determine:

- The effect of SCR on PRB coal in a pulverized coal-fired boiler.
- The effect of the oxidation potential after additional catalyst use.
- The effect of SCR on mercury speciation and capture associated with more conventional wet FGD systems.

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